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APPLICATION NUMBER: 10/083,778

FILING DATE: February 25, 2002

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# FEE TRANSMITTAL for FY 2002

Patent fees are subject to annual revision.

TOTAL AMOUNT OF PAYMENT

(\$)

1,226.00

## Complete if Known

Application Number

Filing Date

First Named Inventor

Shoou-I Wang

Examiner Name

Group Art Unit

Attorney Docket No.

06244 USA

## METHOD OF PAYMENT

1. ☒ The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:

Deposit  
Account  
Number

01-0493

Deposit  
Account  
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Air Products and Chemicals, Inc.

- ☒ Charge Any Additional Fee Required  
Under 37 CFR 1.18 and 1.17

- ☐ Applicant claims small entity status.  
See 37 CFR 1.27

2. ☐ Payment Enclosed:

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## FEE CALCULATION

### 1. BASIC FILING FEE

Large Entity Small Entity

Fee Fee Fee Fee Fee Description

Code (\$) Code (\$) Code (\$) Code (\$)

101 740 201 370 Utility filing fee

106 330 208 165 Design filing fee

107 510 207 255 Plant filing fee

108 740 208 370 Reissue filing fee

114 160 214 80 Provisional filing fee

Fee Paid

740.00

SUBTOTAL (1) (\$)

740

### 2. EXTRA CLAIM FEES

Total Claims 33 -20\*\* = 13 X Fee from below 18 = 234  
Independent Claims 6 -3\*\* = 3 X Fee from below 84 = 252  
Multiple Dependent

Large Entity Small Entity

Fee Fee Fee Fee

Code (\$) Code (\$) Code (\$) Code (\$)

103 18 203 9 Claims in excess of 20

102 84 202 42 Independent claims in excess of 3

104 280 204 140 Multiple dependent claim, if not paid

109 84 209 42 \*\* Reissue independent claims  
over original patent

110 18 210 9 \*\* Reissue claims in excess of 20  
and over original patent

SUBTOTAL (2)

(\$)

486

\*\*or number previously paid, if greater; For Reissues, see above

## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

Large  
Entity

Small  
Entity

Fee Fee Fee Fee

Code (\$) Code (\$) Code (\$)

Fee Description

Fee Paid

105 130 205 85 Surcharge - late filing fee or oath

127 50 227 25 Surcharge - late provisional filing fee or  
cover sheet

139 130 139 130 Non-English specification

147 2,520 147 2,520 For filing a request for ex parte reexamination

112 820\* 112 920\* Requesting publication of SIR prior to  
Examiner action

113 1,840\* 113 1,840\* Requesting publication of SIR after  
Examiner action

115 110 215 55 Extension for reply within first month

116 400 216 200 Extension for reply within second month

117 920 217 460 Extension for reply within third month

118 1,440 218 720 Extension for reply within fourth month

128 1,980 228 980 Extension for reply within fifth month

119 320 219 160 Notice of Appeal

120 320 220 160 Filing a brief in support of an appeal

121 280 221 140 Request for oral hearing

138 1,510 138 1,510 Petition to institute a public use proceeding

140 110 240 55 Petition to revive - unavoidable

141 1,280 241 640 Petition to revive - unintentional

142 1,280 242 640 Utility issue fee (or reissue)

143 460 243 230 Design issue fee

144 620 244 310 Plant issue fee

122 130 122 130 Petitions to the Commissioner

123 50 123 50 Processing fee under 37 CFR 1.17(q)

126 180 126 180 Submission of Information Disclosure Stmt

581 40 581 40 Recording each patent assignment per  
property (times number of properties)

146 740 246 370 Filing a submission after final rejection  
(37 CFR § 1.129(a))

149 740 249 370 For each additional invention to be  
examined (37 CFR § 1.129(b))

179 740 279 370 Request for Continued Examination (RCE)

169 900 169 900 Request for expedited examination  
of a design application

Other fee (specify)

\*Reduced by Basic Filing Fee Paid

SUBTOTAL (3)

(\$)

0

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February 25, 2002

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## TITLE OF THE INVENTION:

A PROCESS AND APPARATUS FOR THE PRODUCTION OF SYNTHESIS GAS

## CROSS-REFERENCE TO RELATED APPLICATIONS

Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT

Not applicable.

## BACKGROUND OF THE INVENTION

5  
10 The present invention relates to a process and apparatus for the production of synthesis gas, particularly for but not necessarily limited to, use in the production of hydrocarbon liquid fuels (e.g. using the Fischer-Tropsch ("F-T") process), methanol (e.g. by catalytic hydrogenation of carbon monoxide), oxo-alcohols and dimethyl ether ("DME").

15 Natural gas may be found in remote locations both on- and offshore. It is generally expensive and impractical to transport natural gas from its source to a distant processing plant. One solution is to convert the gas on-site to a valuable and easily transportable product. In this way, the value of the natural gas may be increased.

20 Natural gas may be converted to synthesis gas (or "syngas") which is a mixture of carbon monoxide and hydrogen. Syngas may be converted to a solid or liquid synthetic fuel ("synfuel") or converted to methanol, oxo-alcohols or DME. For optimum conversion in the F-T process, the ratio of hydrogen to carbon monoxide is preferably about 2 to 1. The conversion products have less volume per unit mass (i.e. have a greater density) than the natural gas. Accordingly, it is more economical to transport conversion products  
25 than a corresponding amount of natural gas.

Syngas may be produced using a heat exchange reforming ("HER") process. A conventional two-step HER process may use natural gas as feedstock and employs a

primary exothermic (or heat-generating) unit producing syngas, e.g. from natural gas and oxygen, coupled with a secondary endothermic (or heat-requiring) unit that uses at least a portion of the heat generated in the primary unit to produce further syngas, e.g. by a reforming reaction of natural gas and steam. In certain HERs, the syngas generated by the HER feeds the primary exothermic unit, while other HERs operate in parallel to the exothermic unit and augment the syngas production therein.

There are several methods of producing syngas from natural gas. Examples of these methods include:

10

(a) Steam-methane reforming ("SMR") which uses an endothermic catalysed reaction between natural gas and steam. There is a need to import carbon dioxide or otherwise remove excess hydrogen to achieve the required ratio of 2 to 1 for the relative proportions of hydrogen and carbon monoxide in the resultant syngas. In many applications (including F-T processes, methanol synthesis and other chemical processes), such an opportunity to import carbon dioxide and/or export any separated excess hydrogen may not be available and/or economical;

15

(b) Partial oxidation ("POX") of natural gas with pure oxygen which achieves a hydrogen to carbon monoxide ratio in the resultant syngas in the range from 1.6 - 1.8 to 1. Imported hydrogen is needed to achieve that required ratio of 2 to 1 for the relative proportions of hydrogen and carbon monoxide in the resultant syngas;

20

(c) Autothermal reforming ("ATR") which uses a partial oxidation burner followed by a catalyst bed with a feed of natural gas, steam and oxygen to produce the required 2 to 1 ratio for the relative proportions of hydrogen and carbon monoxide in the resultant syngas; and

25

(d) Catalytic partial oxidation ("CPO") which is the reaction of natural gas with oxygen over a catalyst that permits flameless partial combustion to hydrogen and carbon monoxide in the required relative proportions in the resultant syngas.

30

For POX, ATR and CPO, the oxidation reaction in the primary heat-generating unit is exothermic and, thus, the syngas is produced at elevated temperature. For

example, POX produces syngas at a temperature of from 1200 to 1400°C, ATR produces syngas at a temperature of from 900 to 1100°C and CPO produces syngas at a temperature of from 1000 to 1100°C.

5           The excess heat generated in these processes may be used to generate steam, for example in waste heat boilers, that can be used in steam turbines to generate power for air separation systems, air compressors and other equipment.

10           The excess heat may be used with additional natural gas and steam in a separate secondary unit to generate further syngas *via* steam-methane reforming. This process is the basis of the generic two-step HER process. In such a process, the high temperature syngas from the primary heat-generating unit is usually introduced to the shell-side of a shell and tube style steam-methane reformer. The tubes may contain conventional steam-methane reforming catalyst over which natural gas and steam react  
15           endothermically to form syngas. The heat from syngas on the shell-side of the reformer is used to drive the endothermic steam-methane reforming reaction. The syngas stream leaving the tubes can be separately collected and used to feed the primary exothermic syngas generator. Preferably, however, the syngas streams leaving the tubes are combined with the syngas on the shell-side to produce syngas having the desired ratio of  
20           hydrogen to carbon monoxide at a temperature of from 500 to 600°C.

          A secondary unit in which reforming takes place over catalyst using heat taken from the primary heat-generating unit is known as a Heat Exchange Reformer. One such example is described in US-A-4919844 (Wang; published on 24th April 1990) and  
25           is called an Enhanced Heat Transfer Reformer (or "EHTR"). The disclosure of this patent is incorporated herein by reference. Other existing HER processes are disclosed in WO-A-98/32817 (Halmo *et al*; published on 30th July 1998), WO-A-00/09441 (Abbot; published on 24th February 2000), WO-A-00/03126 (Fjellhaug *et al*; published on 20th January 2000) and US-A-5362453 (Marsch; published on 8th November 1994). These  
30           disclosures are also incorporated herein by reference.

          An example of an HER process is disclosed in USSN 09/965979 (filed on 27th September 2001 and claiming priority from GB0025150.4 filed on 13th October 2000) and this disclosure is incorporated herein by reference. In this example, a POX reactor

is used in combination with an EHTR. Hydrocarbon fuel gas is reacted with steam and/or oxygen gas in a syngas generation system to produce a syngas product stream. An oxidant gas is compressed to produce a compressed oxidant gas, at least a portion of which is combusted in the presence of combustion fuel gas to produce combustion product gas. The combustion product gas is expanded to produce power and expanded combustion product gas. Heat from the expanded combustion product gas is recovered by using the expanded combustion product gas to heat steam by heat exchange to produce heated steam, at least a portion of which is used to provide at least a portion of any steam requirement for producing the syngas product stream in the syngas generation system. Additionally or alternatively, at least a portion of the oxygen gas is provided using an ASU that is driven by at least a portion of the power generated by the expansion of the combustion product gas.

Syngas product feeding conversion processes will unavoidably contain carbon dioxide. For F-T synfuel processes that use cobalt catalysts, this carbon dioxide behaves like an inert. Whilst it can be vented downstream, the carbon and oxygen capture efficiency of the entire gas to liquid ("GTL") process is lower, which contributes to the greenhouse effect. It is thus desirable to recycle this carbon dioxide to the front-end syngas generator. It is a primary objective of this invention to enable efficient recycle of carbon dioxide and affect its efficient conversion to useful carbon monoxide, while minimizing the amount of such recycle and usage of oxygen feedstock.

Loss of carbon dioxide and methane from natural gas conversion processes is undesirable for several reasons. First, these gases are well known to have "greenhouse gas" properties. Secondly, valuable carbon atoms are being lost to the atmosphere thereby affecting the carbon efficiency and yield of the overall processes. Therefore, it is also an objective of the present invention to reduce the emission level of these greenhouse gases and other pollutants, for example oxides of nitrogen ("NO<sub>x</sub>"), and to recover at least some of the valuable carbon that is usually lost in natural gas conversion processes using HER technology for syngas generation.

In HER processes where hot gas is introduced to the shell-side of an HER, it is undesirable for the temperature of the syngas leaving the primary heat-generating unit to be too high as the mechanical integrity of the HER may be challenged. For example, the

metal of the HER may lose its physical strength and soften. Therefore, it is another objective of the present invention to reduce or eliminate the possibility of problems with the mechanical integrity of the HER resulting from excessive syngas temperature in natural gas conversion processes using HER technology.

5

The POX process can generate syngas with small amounts of solid carbon particles or soot. This soot could foul or erode the heat exchange surfaces in the downstream HER. It is thus another objective of this invention to reduce or eliminate the potential for problems arising for such solid carbon particles.

10

US-A-4731098 (Marsch: published on 15th March 1988) discloses a reformer in which natural gas and steam are reformed to produce syngas. The syngas is then mixed with natural gas and oxygen or air before the mixture leaves the reformer.

15

Water has been used as a diluent in the production of syngas. Examples of such use of water have been disclosed by P. Osterrieth and M. Quintana ("A New Approach to the Production of Custom-made Synthesis Gas Using Texaco's Partial Oxidation Technology"; Texaco Development Corporation; AIChE meeting Presentation, 6th March 1988) and by W. Francis Fong and M. E. Quintana ("HyTEX: A Novel Process for Hydrogen Production"; Texaco Development Corporation; NPRA 89th Annual Meeting, 17th-19th March 1991, San Antonio, Texas)

20

In meeting these objectives, it is also important that any modifications to existing HER processes do not affect adversely the yield of conversion products, the capital and/or operating costs and the level of power usage.

25

#### BRIEF SUMMARY OF THE INVENTION

It has been found that these objectives may be achieved with the introduction of a cooling stream of reactive diluent fluid to the syngas produced in the primary heat-generating unit to produce a cooled mixture of syngas and reactive diluent fluid and the subsequent reaction of at least two of the components of the mixture to either produce further carbon monoxide or to gasify solid carbon particles.

30



Hydrocarbon-containing fuel is exothermically reacted with an oxidant gas comprising molecular oxygen in a first reactor to produce an exothermically-generated syngas product. A stream of reactive diluent fluid is combined with a stream of said exothermically-generated syngas product to produce a reactive mixture and the reactive mixture is reacted in a second reactor to produce a reacted syngas product. If desired, this reacted syngas may be introduced into the secondary reforming unit in an HER process. One advantage of the invention is that the reacted syngas product is cooled before being introduced into the secondary unit thereby avoiding negatively affecting the mechanical integrity of the secondary unit.

If the reactive diluent fluid comprises gases produced downstream in the overall process that would otherwise be vented to the atmosphere or that would have to undergo treatment before venting to atmosphere, the level of pollutant emissions to the environment may be reduced and corresponding cost savings may be achievable from the pollutant gas treatment processes.

Carbon dioxide and hydrogen present in the reactive mixture may be converted into water and valuable carbon monoxide. This conversion is particularly useful when the reactive diluent fluid is carbon dioxide. However, it still has useful application when the reactive diluent fluid is not carbon dioxide but the source of hydrocarbon fuel (e.g. natural gas) contains significant quantities of carbon dioxide. The additional carbon monoxide produced may be used downstream to improve the yield of the natural gas conversion products. If the reactive diluent fluid comprises carbon dioxide that has been recycled from downstream processes then there is a further advantage in that the level of carbon dioxide emission to the environment is reduced.

If the syngas is utilized in an F-T synfuel process, the gas exiting such a downstream process can contain significant amounts of carbon dioxide. Such gas typically also contains unconverted syngas as well as light hydrocarbons. It is particularly advantageous to this invention to recycle such carbon dioxide-comprising gas as the reactive diluent. Such gas can be recycled as diluent without further processing in which case the other components (other than carbon dioxide) would participate in the reaction, increasing the production of desired synfuel. Alternately, the carbon dioxide content of such gas can be isolated in an acid gas removal ("AGR") unit



the exothermically-generated syngas product produced in the primary heat-generating unit and subjecting the reactive mixture to a reverse water gas shift reaction, more carbon dioxide may be converted to useful carbon monoxide. This conversion minimizes the size of the carbon dioxide recycle loops and associated costs. In addition, the reverse shift reaction zone assists in the gasification of any soot in the syngas from a POX-type exothermic unit, mitigating any erosion or fouling concerns in the surfaces of heat exchangers downstream, including HERs, boilers and preheaters. It can also eliminate the requirement of a scrubber that normally accompanies POX processes.

#### 10                   BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

FIGURE 1 is a flowsheet describing one embodiment of the process of the present invention; and

FIGURE 2 is a flowsheet describing a hydrocarbon conversion process in which the process of Figure 1 is integrated with a downstream generic syngas conversion process to produce hydrocarbon liquid fuels or other liquid products.

#### DETAILED DESCRIPTION OF THE INVENTION

According to one aspect of the present invention, there is provided a process for the production of syngas comprising carbon monoxide and molecular hydrogen, said process comprising;

exothermically reacting hydrocarbon-containing fuel an oxidant gas comprising molecular oxygen in a first reactor to produce an exothermically-generated syngas product;

combining a stream of reactive diluent fluid with a stream of said exothermically-generated syngas product to produce a reactive mixture; and

reacting said mixture in a second reactor to produce a reacted syngas product.

The "reactive diluent fluid" includes any diluent fluid that is capable of cooling syngas by direct heat exchange and comprising at least one component that may react with at least one component of the synthesis gas. The "reactive mixture" comprises cooled exothermically generated syngas product and reactive diluent fluid. The "reacted syngas product" includes the product syngas that has undergone a further reaction either to

produce further carbon monoxide or to remove solid carbon particles, e.g. soot, produced as a by-product of the oxidation reaction in the primary heat-generating unit.

5 The hydrocarbon fuel may be a solid or liquid fuel but it is preferably a gas. Natural gas is the preferred fuel. Pure molecular oxygen is preferred as the oxidant gas over an oxidant gas comprising molecular oxygen such as air. Water may be present in the reaction to produce exothermically-generated syngas product (for example, if an ATR process is used). If water is present, it may be used in liquid form in which case it will vaporise immediately upon entry into the first reactor. However, the use of steam is  
10 preferred.

15 An advantage of this invention is that the temperature of the exothermically-generated syngas product is reduced and may be controlled as required for downstream processing. The downstream mechanical integrity problems that may result from the high levels of heat generated in the primary heat-generating unit may be avoided and process operability may be improved by controlling the reduced temperature of the exothermically-generated syngas product.

20 Another advantage of this invention that any solid carbon present in the exothermically-generated syngas product can be at least partially gasified mitigating fouling, erosion or plugging of downstream heat exchangers such as HERs, boilers or preheaters.

25 Where the reactive mixture comprises carbon dioxide, at least a portion of the carbon dioxide may be reacted together with at least a portion of the molecular hydrogen in said mixture over a catalyst in a reverse water gas shift reaction zone to produce a carbon monoxide-enriched syngas product.

30 Where the reactive mixture comprises solid carbon particles, at least a portion of the particles may be gasified by reaction with at least one other component of the mixture in a gasification zone to produce a solid carbon-depleted syngas product. The gasification reaction preferably occurs on the surface of a gasification reaction support structure and may be catalysed.

The process preferably further comprises endothermically reforming hydrocarbon-containing fuel gas with steam over a catalyst in a heat exchange reformer to produce a heat exchange-reformed syngas product. At least a portion of the heat required in the generation of said heat exchange-reformed syngas product is obtained by recovering heat from said reacted syngas product thereby cooling the reacted syngas product. Use of this heat in this way provides further overall cooling of the syngas. The heat exchange-reformed syngas product may be combined with the reacted syngas product prior to heat recovery.

When the reactive diluent fluid is a gas, the exothermically-generated syngas product is first cooled *via* sensible heat exchange. When the reactive diluent fluid is a liquid, initial cooling occurs *via* vaporisation and sensible heat exchange. The reactive diluent fluid may be recovered and recycled from downstream processing of syngas. The reactive diluent fluid may promote the gasification of any solid carbon particles or soot present in the reactive mixture. The reactive diluent fluid may be imported from an external source.

The reactive diluent fluid preferably comprises carbon dioxide. An advantage of using carbon dioxide as the diluent is that it may be readily converted to more useful carbon monoxide *via* a reverse water-gas shift reaction (see reaction (III)), resulting in more carbon monoxide being available for downstream processing. In addition, if the carbon dioxide has been recycled from downstream processes, the potential emission level of this greenhouse gas is reduced.

The reactive diluent fluid may comprise carbon dioxide separated, e.g. by acid gas recovery and recycled from downstream syngas or recovered and recycled from downstream processing of syngas. Alternately, the residual gas from a GTL reactor comprising carbon dioxide can be recycled without processing in an AGR unit. The reactive diluent may comprise the products of a combustion process which would contain a significant quantity of carbon dioxide. The combustion products may be selected from the group consisting of combustion furnace flue gases and gas turbine exhaust gas. The reactive diluent fluid may comprise carbon dioxide imported from an external source. For certain applications, the reactive diluent fluid may comprise carbon dioxide and methane either alone or together with other hydrocarbon(s) such as ethane, propane,

butane, pentane, hexane and/or their isomers. In a typical F-T based GTL process, the diluent may be a residual effluent of the reactor after separation of synfuel and water. In this case, it would comprise of carbon dioxide, unreacted carbon monoxide and molecular hydrogen, low molecular weight paraffins, olefins and oxygenates. The  
5 recycling of these gases increases their utilization and increases the overall GTL process efficiency.

The reactive diluent fluid may comprise molecular hydrogen. The injection of hydrogen into the first syngas product pushes the position of the equilibrium in reaction  
10 (III) in a reverse water gas shift reaction towards the carbon monoxide product side. This effect is advantageous because it promotes the conversion of carbon dioxide to carbon monoxide.

The use of carbon dioxide or molecular hydrogen as diluent is advantageous as  
15 both gases are capable of promoting the gasification of carbon components in the mixture of cooled exothermically-generated syngas product and reactive diluent fluid.

The reactive diluent fluid may comprise water. The water may be in the form of liquid water or steam or may comprise a combination of liquid water and steam. The  
20 injection of water is primarily to promote the gasification of carbon components in the mixture of cooled exothermically-generated syngas product and reactive diluent fluid.

The reacted syngas product from the reformer is preferably used in a downstream conversion process to produce conversion products selected from the group  
25 consisting of hydrocarbon liquid fuels, methanol, DME and oxo-alcohols.

In a second aspect of the present invention, there is provided a process for the production of syngas comprising carbon monoxide and molecular hydrogen, said process comprising;

30 exothermically reacting hydrocarbon-containing fuel with an oxidant gas comprising molecular oxygen in a first reactor to produce an exothermically-generated syngas product;

cooling an effluent stream of said exothermically-generated syngas product by combining reactive diluent fluid with said stream to produce a mixture comprising cooled

exothermically-generated syngas product and reactive diluent fluid, said mixture further comprising at least one component selected from the group consisting of carbon dioxide and solid carbon particles;

5 reacting together carbon dioxide in said mixture with molecular hydrogen in said mixture to produce a carbon monoxide-enriched syngas product; and/or  
gasifying solid carbon particles in said mixture with at least one other component in said mixture to produce a solid carbon-depleted syngas product.

10 The step of the process to produce solid carbon-depleted syngas can be carried out instead of the step to produce carbon monoxide-enriched syngas and vice versa. Alternatively, the two steps can be carried out either sequentially or simultaneously.

15 In a third aspect of the present invention, there is provided a process for the production of syngas comprising carbon monoxide and molecular hydrogen, said process comprising:

exothermically reacting hydrocarbon-containing fuel gas with an oxidant gas comprising molecular oxygen in a first reactor to produce a first syngas product;  
cooling an effluent stream of said first syngas product by combining reactive diluent fluid comprising carbon dioxide with said stream to produce a mixture of cooled  
20 first syngas product and reactive diluent fluid;  
reacting at least a portion of the carbon dioxide in said mixture with at least a portion of the molecular hydrogen in said mixture over a catalyst in a reverse water gas shift reaction zone to produce a carbon monoxide-enriched syngas product;  
endothermically reforming hydrocarbon-containing fuel gas with steam over a  
25 catalyst in a heat exchange reformer to produce a second syngas product; and  
combining at least a portion of said second syngas product with at least a portion of the carbon monoxide-enriched syngas product to produce a combined syngas product,  
wherein at least a portion of the heat generated in the exothermic reaction producing  
30 said first syngas product is used to drive the endothermic reforming reaction.

In a fourth aspect of the present invention, there is provided apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen, said apparatus comprising:

a first reactor in which hydrocarbon-containing fuel is reacted exothermically with an oxidant gas comprising molecular oxygen to produce an exothermically-generated syngas product;

5 conduit means for removing an effluent stream of said exothermically-generated syngas product from the first reactor;

means for combining a stream of reactive diluent fluid with said effluent stream to produce a reactive mixture; and

a second reactor in which said mixture reacts to produce a reacted syngas product.

10 The first reactor is preferably selected from the group consisting of a POX reactor, an ATR or a CPO reactor.

15 Where the reactive mixture comprises carbon dioxide, the second reactor preferably has a reverse water gas shift reaction zone in which at least a portion of the carbon dioxide and at least portion of the molecular hydrogen in the reactive mixture are reacted together over a catalyst to produce a carbon monoxide-enriched syngas.

20 Where the reactive mixture comprises solid carbon particles, the second reactor may have a gasification reaction zone in which at least a portion of the solid carbon particles is gasified by reaction with at least one other component of the reactive mixture to produce a solid carbon-depleted syngas.

25 The apparatus preferably further comprises a heat exchange reformer in which hydrocarbon-containing fuel gas is reformed endothermically with steam over a catalyst to produce a heat exchange-reformed syngas product, wherein at least a portion of the heat required in the generation of said heat exchange-reformed syngas product is obtained by recovering heat from said reacted syngas product thereby cooling the reacted syngas product.

30 The reformer is preferably a shell and tube style reformer in which the endothermic reforming reaction occurs within the tubes and the reacted syngas product is introduced to the shell-side. Most preferably, the reformer is an EHTR.



In a fifth aspect of the present invention, there is provided apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen, said apparatus comprising:

- 5 a first reactor in which hydrocarbon-containing fuel is reacted exothermically with an oxidant gas comprising molecular oxygen to produce an exothermically-generated syngas product;
- conduit means for removing an effluent stream of said exothermically generated syngas product from the first reactor;
- 10 means for combining reactive diluent gas comprising carbon dioxide with said effluent stream to produce a mixture comprising cooled first syngas product and reactive diluent gas, said mixture further comprising at least one component selected from the group consisting of carbon dioxide and solid carbon particles;
- a reverse water gas shift reaction zone in which carbon dioxide in said mixture is reacted together with molecular hydrogen in said mixture over a catalyst to produce a carbon
- 15 monoxide-enriched syngas product; and/or
- a gasification reaction zone in which solid carbon particles in said mixture are gasified with at least one other component in said mixture to produce a solid carbon-depleted syngas product.

20 In a sixth aspect of the present invention, there is provided apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen, said apparatus comprising:

- a first reactor in which hydrocarbon-containing fuel gas is reacted exothermically with an oxidant gas comprising molecular oxygen to produce a first syngas product;
- 25 conduit means for removing an effluent stream of said first syngas product from the first reactor;
- means for combining reactive diluent gas comprising carbon dioxide with said effluent stream to produce a mixture of cooled first syngas product and reactive diluent gas;
- a reverse water gas shift reaction zone in which at least a portion of the carbon dioxide in
- 30 said mixture is reacted with at least a portion of the molecular hydrogen in said mixture over a catalyst to produce a carbon monoxide-enriched syngas product; and
- a heat exchange reformer in which hydrocarbon-containing fuel gas is reformed endothermically with steam over a catalyst to produce a second syngas product and in which at least a portion of said second syngas product is combined with at least a portion

of said carbon monoxide-enriched syngas product to produce a combined syngas product, wherein at least a portion of the heat generated in the exothermic reaction producing said first syngas product is used to drive the endothermic reforming reaction.

5       The first reactor is preferably a POX reactor as this reactor produces the highest temperature syngas (when compared with ATR and CPO) and the higher the temperature of the syngas from the primary heat-generating unit, the higher the conversion of carbon dioxide in the reactive diluent and the better the efficiency of downstream HER processing. The POX reactor is preferably used in combination with  
10       an EHTR as the heat exchange reformer.

#### EXAMPLE

15       Referring to Figure 1, a stream 2 of natural gas is preheated by indirect heat exchange 8, hydrodesulfurized as required, and divided into a first portion 4 and a second portion 6. The first portion 4 is introduced into a POX reactor 12. A stream 14 of oxygen is pre-heated by indirect heat exchange 16 and the pre-heated oxygen stream 18 is also fed to the POX reactor 12. The natural gas and the oxygen are reacted together in the POX reactor 12 to produce first syngas product. A stream 20 of first syngas  
20       product is removed from the POX reactor 12 at a temperature of from 1200 to 1400°C.

25       A stream 22 comprising carbon dioxide is introduced to and cools the first syngas product stream 20. The cooled stream 24 is fed to a reverse water gas shift reactor 26 in which at least a portion of the carbon dioxide from the cooled stream 24 is reacted with at least a portion of the hydrogen from the cooled stream 24 to produce carbon monoxide and water. The catalytic reaction is endothermic and, thus, a further cooling effect on the syngas is observed. A stream 28 of carbon monoxide-enriched syngas is removed from the reverse water gas shift reactor 26 and introduced to the shell-side of an EHTR 30.

30       A stream 32 of steam is introduced to the second portion 6 of the natural gas and the combined stream 34 is pre-heated by indirect heat exchange 36. The pre-heated combined stream 38 is introduced to the tube-side of the EHTR 30. The tubes of the EHTR 30 contain conventional steam-methane reforming catalyst and the natural gas

and the steam react to form second syngas product. Heat from the shell-side of the EHTR 30 provided at least in part by the carbon monoxide-enriched syngas, is used to drive the endothermic catalytic steam-methane reforming reaction.

5 The second syngas product leaving the tubes of the EHTR 30 is combined with the first syngas product to form a combined syngas product. A stream 40 of combined syngas product is removed for downstream processing, in particular for the synthesis of hydrocarbon liquid fuels (e.g. by the F-T process), methanol (e.g. by the catalytic hydrogenation of carbon monoxide), oxo-alcohols and DME.

10

Table 1 contains data for the composition of various streams in the process of Figure 1 calculated in a computer simulation.

[illegible]

STREAM ID STREAM	2 NG FEED	4 NG TO POX	6 NG TO EHTR	18 POX O2	20 POX OUT	22 FT OFFGAS	24 QUENCH ED	28 CATBEDO UT	38 EHTR FEED	40 EHTR OUT
Temperature F	60	685	685	449.3	2450	100	2269.7	2185.7	950	1094.2
Pressure psia	515	494	494	460	412	600	412	412	484	412
Mole Flow lbmol/hr	18542	14471	4653	9187	43416	2301	45717	45908	14499	68238
Enthalpy MMBtu/hr	-625.0	-371.6	-119.5	24.3	-348.3	-390.9	-739.2	-739.2	-1055.0	-1814.0
COMPONENTS										
Mole Flow lbmol/hr										
H2		440.4	141.6		25213.8		25213.8	23774.9	141.6	36219.7
C1	17564.4	13290.9	4273.5		200.1		200.1	104.3	4273.5	877.1
C2	585.9	443.4	142.6						142.6	
C3	100.1	75.8	24.4						24.4	
C4	33.4	25.3	8.1						8.1	
C5	11.1	8.4	2.7						2.7	
C6	7.4	5.6	1.8						1.8	
CD	131.6	99.6	32.0							
CM					741.7	2300.9	3042.5	1316.1	32.0	2139.7
WA					13739.6		13739.6	15561.9		18686.0
O2				9140.6	3393.3		3393.3	5023.9	9845.9	10162.6
AR				45.9	45.9		45.9	45.9		45.9
N2	107.5	81.4	26.2		81.4		81.4	81.4	26.2	107.5
Mole percent										
H2		3.00%	3.00%		58.10%		55.20%	51.80%	1.00%	53.10%
C1	94.70%	91.80%	91.80%		0.50%		0.40%	0.20%	29.50%	1.30%
C2+	PRESENT	PRESENT	PRESENT						PRESENT	
CD	0.70%	0.70%	0.70%		1.70%	100.00%	6.70%	2.90%	0.20%	3.10%
CM					31.60%		30.10%	33.90%		27.40%
WA					7.80%		7.40%	10.90%	67.90%	14.90%
O2				99.50%						
AR				0.50%	0.10%		0.10%	0.10%		0.10%
N2	0.60%	0.60%	0.60%		0.20%		0.20%	0.20%	0.20%	0.20%

Referring now to Figure 2, a syngas generation system 42 of the type depicted in Figure 1 is fed by a stream 2 of hydrocarbon fuel gas, a stream 14 of oxygen or air and a stream 32 of steam. A stream 40 of syngas is removed from the syngas generation system 42 and fed to a syngas conversion system 44. The syngas conversion system 44 may use an F-T process to synthesize liquid hydrocarbons or involve the synthesis of methanol, DME or oxo-alcohols. A stream 46 of raw conversion product is removed from the syngas conversion system 44 and upgraded and refined 50 to produce the liquid products 52.

A stream 22 of reactive diluent gas is recycled from the syngas conversion system 44 to the syngas generation system 42. A recycle stream 54 may also be taken from the product upgrading and refining process 50.

It will be appreciated that the invention is not restricted to the details described above with reference to the preferred embodiments but that numerous modifications and variations can be made without departing from the spirit or scope of the invention as defined in the following claims.

## CLAIMS

1. A process for the production of synthesis gas ("syngas") comprising carbon monoxide and molecular hydrogen, said process comprising;  
5                    exothermically reacting hydrocarbon-containing fuel with an oxidant gas comprising molecular oxygen in a first reactor to produce an exothermically-generated syngas product;  
                     combining a stream of reactive diluent fluid with a stream of said exothermically-generated syngas product to produce a reactive mixture; and  
10                    reacting said mixture in a second reactor to produce a reacted syngas product.
2. The process according to Claim 1, wherein the oxidant gas consists of molecular oxygen.  
15
3. The process according to Claim 1, wherein the hydrocarbon fuel is reacted with the oxidant gas in the presence of water.
4. The process according to Claim 1 wherein the reactive mixture comprises carbon dioxide, at least a portion of which is reacted together with at least a portion of the molecular hydrogen in said mixture over a catalyst in a reverse water gas shift reaction zone to produce a carbon monoxide-enriched syngas product.  
20
5. The process according to Claim 1 wherein the reactive mixture comprises solid carbon particles, at least a portion of which is gasified by reaction with at least one other component of the mixture in a gasification zone to produce a solid carbon-depleted syngas product.  
25
6. The process according to Claim 1 further comprising endothermically reforming hydrocarbon-containing fuel gas with steam over a catalyst in a heat exchange reformer to produce a heat exchange-reformed syngas product, wherein at least a portion of the heat required in the generation of said heat exchange-reformed syngas product is obtained by recovering heat from said reacted syngas product thereby cooling the reacted syngas product.  
30

7. The process according to claim 6 wherein said heat exchange-reformed syngas product is combined with said reacted syngas product prior to heat recovery.

5 8. The process according to Claim 1 wherein the reactive diluent fluid is a gas thereby cooling the exothermically-generated syngas product via sensible heat exchange.

10 9. The process according to Claim 1 wherein the reactive diluent fluid is a liquid thereby cooling the exothermically-generated syngas product *via* vaporisation and sensible heat exchange.

15 10. The process according to Claim 1 wherein the reactive diluent fluid is recovered and recycled from downstream processing of syngas.

11. The process according to Claim 1 wherein the reactive diluent fluid comprises carbon dioxide.

20 12. The process according to Claim 11 wherein the reactive diluent fluid comprises carbon dioxide separated and recycled from downstream syngas.

13. The process according to Claim 11 wherein the reactive diluent fluid comprises the products of a combustion process.

25 14. The process according to Claim 13 wherein the combustion products are selected from the group consisting of combustion furnace flue gases and gas turbine exhaust gas.

15. The process according to Claim 11 wherein the reactive diluent fluid comprises carbon dioxide imported from an external source.

30 16. The process according to Claim 11 wherein the reactive diluent fluid further comprises a component selected from the group consisting of methane and other hydrocarbon(s).

17. The process according to Claim 1 wherein the reactive diluent fluid comprises molecular hydrogen.
18. The process according to Claim 1 wherein the reactive diluent fluid comprises water.
19. The process according to Claim 18 wherein the water is in the form of liquid water.
20. The process according to Claim 18 wherein at least a portion of the water is in the form of steam.
21. The process according to Claim 1 wherein the reacted syngas product is used in a downstream conversion process to produce conversion products selected from the group consisting of hydrocarbon liquid fuels, methanol, DME and oxo-alcohols.
22. A process for the production of syngas comprising carbon monoxide and molecular hydrogen, said process comprising:
- exothermically reacting hydrocarbon-containing fuel with an oxidant gas comprising molecular oxygen in a first reactor to produce an exothermically-generated syngas product;
  - cooling an effluent stream of said exothermically-generated syngas product by combining reactive diluent fluid with said stream to produce a mixture comprising cooled exothermically-generated syngas product and reactive diluent fluid, said mixture further comprising at least one component selected from the group consisting of carbon dioxide and solid carbon particles;
  - reacting together carbon dioxide in said mixture with molecular hydrogen in said mixture to produce a carbon monoxide-enriched syngas product; and/or
  - gasifying solid carbon particles in said mixture with at least one other component in said mixture to produce a solid carbon-depleted syngas product.
23. A process for the production of syngas comprising carbon monoxide and molecular hydrogen, said process comprising:



exothermically reacting hydrocarbon-containing fuel gas with an oxidant gas comprising molecular oxygen in a first reactor to produce a first syngas product;

5       cooling an effluent stream of said first syngas product by combining reactive diluent fluid comprising carbon dioxide with said stream to produce a mixture of cooled first syngas product and reactive diluent fluid;

10       reacting at least a portion of the carbon dioxide in said mixture with at least a portion of the molecular hydrogen in said mixture over a catalyst in a reverse water gas shift reaction zone to produce a carbon monoxide-enriched syngas product;

      endothermically reforming hydrocarbon-containing fuel gas with steam over a catalyst in a heat exchange reformer to produce a second syngas product; and

15       combining at least a portion of said second syngas product with at least a portion of the carbon monoxide-enriched syngas product to produce a combined syngas product,

wherein at least a portion of the heat generated in the exothermic reaction producing said first syngas product is used to drive the endothermic reforming reaction.

20   24.   Apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen, said apparatus comprising:

      a first reactor in which hydrocarbon-containing fuel is reacted exothermically with an oxidant gas comprising molecular oxygen to produce an exothermically-generated syngas product;

25       conduit means for removing an effluent stream of said exothermically-generated syngas product from the first reactor;

      means for combining a stream of reactive diluent fluid with said effluent stream to produce a reactive mixture; and

30       a second reactor in which said mixture reacts to produce a reacted syngas product.

25.   Apparatus according to Claim 24 wherein the first reactor is selected from the group consisting of a partial oxidation ("POX") reactor, an autothermal reformer ("ATR") and a catalytic partial oxidation ("CPO") reactor.

26. Apparatus according to Claim 24 wherein the reactive mixture comprises carbon dioxide and the second reactor has a reverse water gas shift reaction zone in which at least a portion of the carbon dioxide and at least portion of the molecular hydrogen in said mixture are reacted together over a catalyst to produce a carbon monoxide-enriched syngas product.

27. Apparatus according to Claim 24 wherein the reactive mixture comprises solid carbon particles and the second reactor has a gasification reaction zone in which at least a portion of the solid carbon particles is gasified by reaction with at least one other component of the mixture to produce a solid carbon-depleted syngas product.

28. Apparatus according to Claim 24 further comprising a heat exchange reformer in which hydrocarbon-containing fuel gas is reformed endothermically with steam over a catalyst to produce a heat exchange-reformed syngas product, wherein at least a portion of the heat required in the generation of said heat exchange-reformed syngas product is obtained by recovering heat from said reacted syngas product thereby cooling the reacted syngas product.

29. Apparatus according to Claim 28 wherein the heat exchange reformer is a shell and tube style reformer in which the endothermic reforming reaction occurs within the tubes and the reacted syngas product is introduced to the shell-side.

30. Apparatus according to Claim 28 wherein the reformer is an enhanced heat transfer reformer ("EHTR").

31. Apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen, said apparatus comprising:

a first reactor in which hydrocarbon-containing fuel is reacted exothermically with an oxidant gas comprising molecular oxygen to produce an exothermically-generated syngas product;

conduit means for removing an effluent stream of said exothermically generated syngas product from the first reactor;

means for combining reactive diluent gas comprising carbon dioxide with said effluent stream to produce a mixture comprising cooled first syngas product

and reactive diluent gas, said mixture further comprising at least one component selected from the group consisting of carbon dioxide and solid carbon particles;

a reverse water gas shift reaction zone in which carbon dioxide in said mixture is reacted together with molecular hydrogen in said mixture over a catalyst to produce a carbon monoxide-enriched syngas product; and/or

a gasification reaction zone in which solid carbon particles in said mixture are gasified with at least one other component in said mixture to produce a solid carbon-depleted syngas product.

32. Apparatus for the production of syngas comprising carbon monoxide and molecular hydrogen, said apparatus comprising:

a first reactor in which hydrocarbon-containing fuel gas is reacted exothermically with an oxidant gas comprising molecular oxygen to produce a first syngas product;

conduit means for removing an effluent stream of said first syngas product from the first reactor;

means for combining reactive diluent gas comprising carbon dioxide with said effluent stream to produce a mixture of cooled first syngas product and reactive diluent gas;

a reverse water gas shift reaction zone in which at least a portion of the carbon dioxide in said mixture is reacted with at least a portion of the molecular hydrogen in said mixture over a catalyst to produce a carbon monoxide-enriched syngas product; and

a heat exchange reformer in which hydrocarbon-containing fuel gas is reformed endothermically with steam over a catalyst to produce a second syngas product and in which at least a portion of said second syngas product is combined with at least a portion of said carbon monoxide-enriched syngas product to produce a combined syngas product, wherein at least a portion of the heat generated in the exothermic reaction producing said first syngas product is used to drive the endothermic reforming reaction.

33. Apparatus according to Claim 32 wherein the first reactor is a partial oxidation ("POX") reactor and the reformer is an EHTR.

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## ABSTRACT OF THE DISCLOSURE

5            Reactive diluent fluid is introduced into a stream of synthesis gas (or "syngas")  
produced in a heat-generating unit such as a partial oxidation ("POX") reactor to cool the  
syngas and form a mixture of cooled syngas and reactive diluent fluid. Carbon dioxide  
and/or carbon components and/or hydrogen in the mixture of cooled syngas and reactive  
diluent fluid is reacted with at least a portion of the reactive diluent fluid in the mixture to  
10        produce carbon monoxide-enriched syngas which may be fed into a secondary reformer  
unit such as an enhanced heat transfer reformer in a heat exchange reformer process.  
An advantage of the invention is that problems with the mechanical integrity of the  
secondary unit arising from the high temperature of the syngas from the heat-generating  
unit are avoided.

15

<b>DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)</b>  <input checked="" type="checkbox"/> Declaration Submitted with Initial Filing      OR <input type="checkbox"/> Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)	<b>Attorney Docket Number</b>	06244 USA
	<b>First Named Inventor</b>	Shouu-I Wang
	<b>COMPLETE IF KNOWN</b>	
	<b>Application Number</b>	/
	<b>Filing Date</b>	
	<b>Group Art Unit</b>	
	<b>Examiner Name</b>	

As a below named inventor, I hereby declare that:

My residence, mailing address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

A Process and Apparatus For The Production of Synthesis Gas

(Title of the Invention)

the specification of which

☒ is attached hereto

OR

☐ was filed on (MM/DD/YYYY)

as United States Application Number or PCT International

Application Number

and was amended on (MM/DD/YYYY)

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
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☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

[Page 1 of 2]


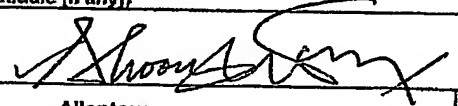
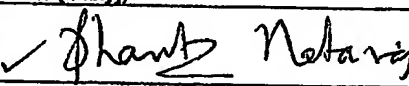
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NAME OF SOLE OR FIRST INVENTOR :		<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle (if any)) Shouu-l		Family Name or Surname Wang			
Inventor's Signature 		Date		✓ 21 Feb, 2002	
Residence: City Allentown		PA State		USA Country	
Mailing Address		4011 Winchester Road			
Mailing Address		Allentown PA 18104 USA City State ZIP Country			
NAME OF SECOND INVENTOR:		<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle (if any)) Shankar		Family Name or Surname Nataraaj			
Inventor's Signature ✓ 		Date		✓ 21 Feb, 2002	
Residence: City Allentown		PA State		USA Country	
Mailing Address		1012 S. Hillview Drive			
Mailing Address		Allentown PA 18103 USA City State ZIP Country			
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## DECLARATION

ADDITIONAL INVENTOR(S)  
Supplemental Sheet  
Page 1 of 1

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any])		Family Name or Surname	
John Michael		Repasky	
Inventor's Signature <i>John Michael Repasky</i>		Date <i>21 Feb 2002</i>	
Residence: City	PA State	USA Country	USA Citizenship
Mailing Address 329 Barn Swallow Lane			
Mailing Address			
City	PA State	ZIP 18104	USA Country
Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any])		Family Name or Surname	
Inventor's Signature		Date	
Residence: City	State	Country	Citizenship
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Given Name (first and middle [if any])		Family Name or Surname	
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**STATEMENT UNDER 37 CFR 3.73(b)**

Applicant/~~Patent Owner~~: Shoou-I Wang

Application No./Patent No.: \_\_\_\_\_ Filed/Issue Date: \_\_\_\_\_

Entitled: A Process and Apparatus For The Production of Synthesis Gas

Air Products and Chemicals, Inc., a corporation  
(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that it is:

1. ☒ the assignee of the entire right, title, and interest; or  
2. ☐ an assignee of less than the entire right, title and interest.  
The extent (by, percentage) of its ownership interest is \_\_\_\_\_ %

In the patent application/patent identified above by virtue of either:

A. ☒ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel \_\_\_\_\_, Frame \_\_\_\_\_, or for which a copy thereof is attached.

OR

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as shown below:

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[NOTE: A separate copy (i.e., the original assignment document or a true copy of the original document) must be submitted to Assignment Division in accordance with 37 CFR Part 3, if the assignment is to be recorded in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

25 February 2002  
Date

William F. Marsh

Typed or printed name

William F. Marsh  
Signature

Assistant General Counsel, Patents

Title

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Application Number	
Filing Date	
First Named Inventor	Shoou-I Wang
Title	A Process and Apparatus For The...
Group Art Unit	
Examiner Name	
Attorney Docket Number	06244 USA

I hereby appoint:

☒ Practitioners at Customer Number

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☐ Practitioner(s) named below:



**23543**

Air Products and Chemicals, Inc.

Name	Reg.

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☐ Applicant/Inventor.

☒ Assignee of record of the entire interest. See 37 CFR 3.71.  
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

### SIGNATURE of Applicant or Assignee of Record

Name	William F. Marsh
Signature	<i>William F. Marsh</i>
Date	25 February 2002

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below.

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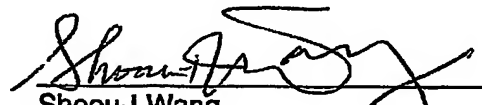
For value received, we, Shouu-I Wang, Shankar Nataraj, and John Michael Repasky, hereby sell, assign, and transfer to **AIR PRODUCTS AND CHEMICALS, INC.**, a corporation of the State of Delaware, having an office at 7201 Hamilton Boulevard, Allentown, PA 18195-1501, the entire right, title, and interest in and to the invention relating to

**A Process and Apparatus For The Production of Synthesis Gas**

described in our application for Letters Patent of the United States (identified by Docket No. 06244 USA) executed of even date herewith, in and to all Letters Patent which may be issued upon said application, in and to any divisional or reissue applications based thereon, and in and to all Letters Patent upon said invention or improvements which may be granted in foreign countries. We hereby also assign and convey to said **AIR PRODUCTS AND CHEMICALS, INC.**, all the rights accruing to us by virtue of the International Convention for the Protection of Industrial Property (Art. 4), including the right to apply for and to have patents issued in its own name.

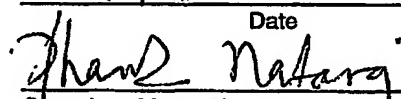
And we hereby authorize and request the Commissioner of Patents and Trademarks of the United States and the Officials of the Patent Offices of all other countries to issue the Letters Patent of their respective countries to said **AIR PRODUCTS AND CHEMICALS, INC.**, as assignee of the entire right, title, and interest in and to the same.

And we hereby promise and agree to execute all papers and perform all acts necessary to secure to and vest in said **AIR PRODUCTS AND CHEMICALS, INC.**, its successors and assigns, the rights conveyed as herein set forth.

 (L.S.)  
Shouu-I Wang

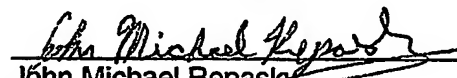
21 Feb. 2002

Date

 (L.S.)  
Shankar Nataraj

21 Feb 2002

Date

 (L.S.)  
John Michael Repasky

21 Feb 2002

Date

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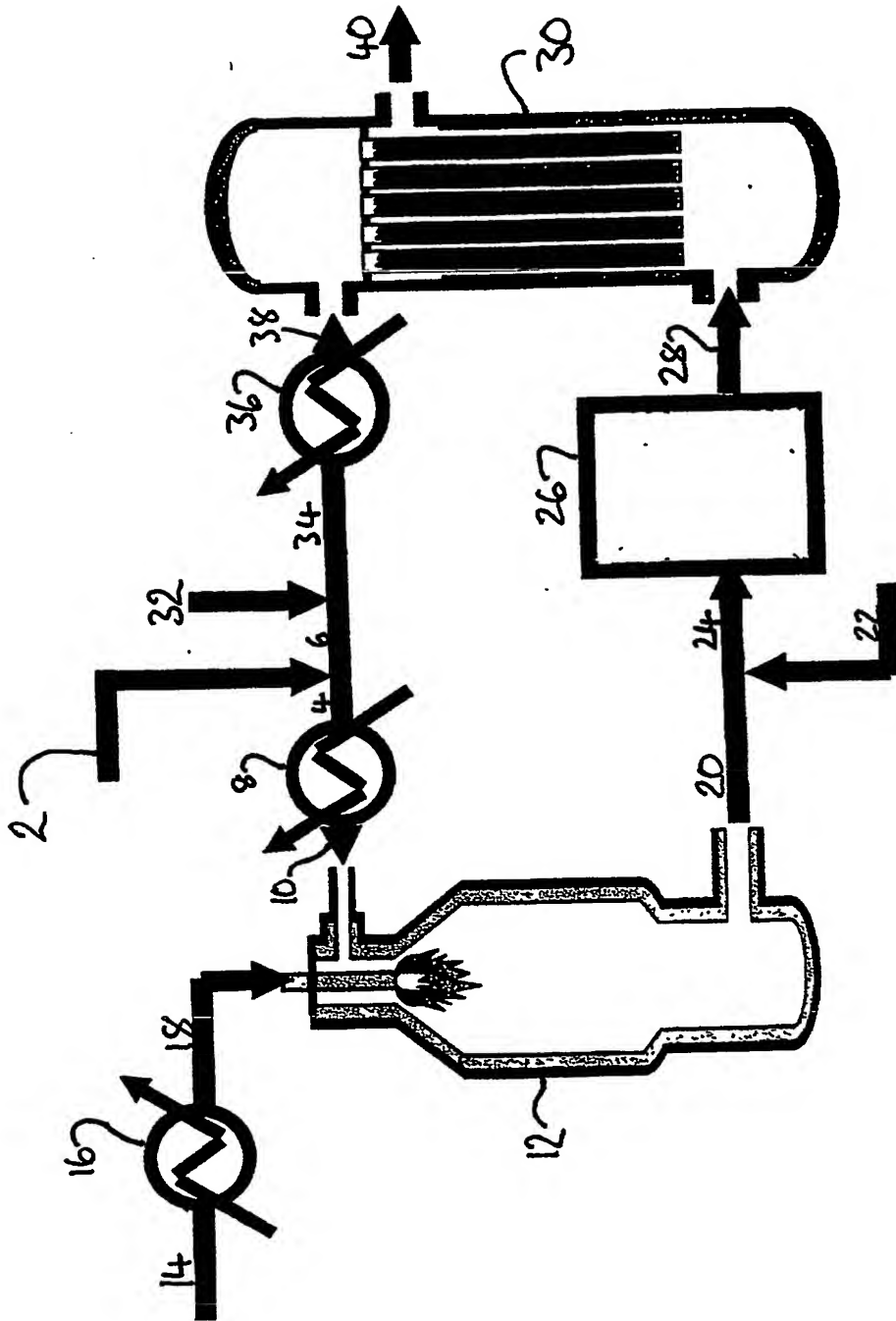


FIGURE 1

FIGURE 2

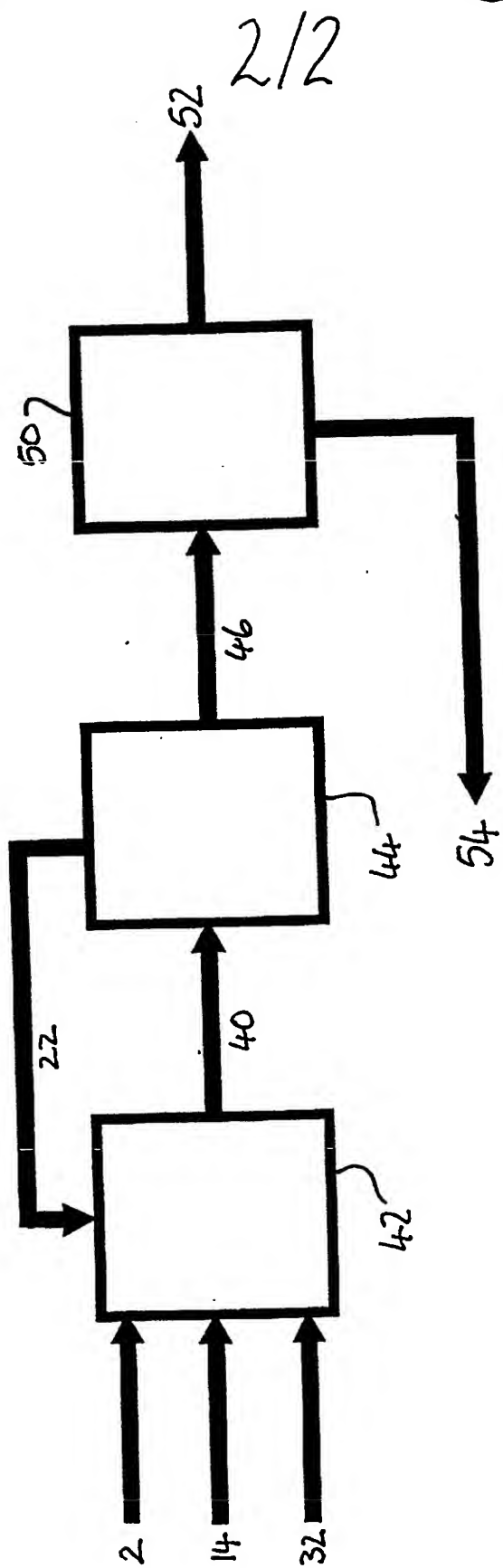


FIGURE 2

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